USSR/Phys. Chemistry, Thermodynamics, Thermochemistry, Equilibriums   B-8
    Phys. Chem. Anal-is, Phase-Transitions

Abs Jour : Ref Zhur - Khimiya, No 7, 1957, 22263

Author   : S. A. Shchukarev, M. A. Oranskaya, V. M. Tsintsius
Inst   : Not given
Title   : Thermic dissociation of gold chlorides

Orig Pub : Zh. neorgan. khimii, 1956, No 5, 881-886

Abstract : Dissociation pressures of $AuCl_3$ are determined by static method
           in the range 150-247° C for the reaction $AuCl_3 \rightleftarrows AuCl + Cl_2$
           (gp_{Cl_2}(at) = 8.73-4547/T) and AuCl in the range 150-255° C for
           the reaction $2AuCl \rightleftarrows Au + Cl_2$ (lgp_{Cl_2}(at) = 6.23-3483/T). Varia-
           tions of entropy (in entropy units) are calculated for indica-
           ted reactions, respectively : $\Delta S = 38.5 \pm 1.5$ and 30 ± 3 and the
           formation of heat (in kcal/mole) of $AuCl_3 \Delta H = -27 \pm I$ and
           $AuCl \Delta H = 8.0 \pm 1.0$. Computation of free energy variations shows
           that at $T < 450°K$ AuCl is metastable on account of freezing of
           disproportionation reaction $3AuCl = AuCl_3 + 2Au$. Attempts to
           obtain a hypothetical compound $AuCl_2$ remained ineffective.

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Card 1/1

SHCHUKAREV, S A.

C

USSR/Inorganic Chemistry   Complex Compounds.

Abs Jour   : Referat. Zhurnal Khimiya, No 6, 1957, 18861

Author   : S.A. Shchukarev, O.A. Lobaneva.
Inst   : Leningrad University
Title   : Concerning Application of Spectrophotometry as
               Method of Studying Complex Formation in Solutions.

Orig Pub   : Vestn. Leningr. Un-ta, 1956, No 16, 64-73.

Abstract   : The methods of Ostromyslenskiy-Zhob, Vosborgh and
               Cooper (Vosborgh W.C., Cooper, G.R., J. Amer. Chem.
               Soc., 1941, 63, 437), Bent and French (Bent H.E.,
               French C.L., J. Amer. Chem. Soc., 1941, 63, 568) of
               the spectrophotometric study of complex formation in
               solutions and Bjerrum's method of formation function
               were discussed. In the opinion of the authors, the
               last method is more advantageous than the first three,
               because it can be used at a simultaneous formation of
               several complexes in the solution and allows to es-
               tablish their distribution. A combined spectrophoto-

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Card 1/2

C

metric method is proposed. The presence of the colo-
wise non-complicated hydrolysis is proved with colo-
metric titration according to Bjerrum and the poly-
merisation of the complex formation, after which they
measure the absorption curves of solutions, in which
one or another complex is contained in a large quan-
tity (the value of the formation function π is a whole
number). The complex formation in the system acetone
(Ac) + CoBr$_2$ + LiBr was studied. A simple stepwise
complex formation is accomplished in this system only
in diluted solutions at a concentration of Co < 0.0014
M. It is shown that 5 complexes are formed: Li$_4$
(CoBr$_6$), Li$_2$(CoBr$_4 \cdot$2Ac), Li(CoBr$_3 \cdot$3Ac), (CoBr$_2 \cdot$4Ac)
and CoBr$\cdot$5Ac)Br, to which the absorption maxima at
720, 700, 670, 640 and 580 m$\cdot$ correspond. It seems
that the complex Li$_3$(CoBr$_5 \cdot$Ac) is absent owing to the
disproportionization of (CoBr$_4 \cdot$2Ac)$^{2-}$ $\leftarrow$ (CoBr$_5 \cdot$Ac)$^{3-}$ $\rightarrow$
$\rightarrow$ (CoBr$_6$)$^{4-}$.

-35-

Card 2/2

SHCHUKAREV, S.A.

Enthalpy of formation for compounds of zinc with anti- mony. S. A. Shchukarev, M. P. Morozova, and Yu. P. Sapozhnikov. *J. Gen. Chem. U.S.S.R.* 26, 321-3(1956) (English translation).—See *C.A.* 50, 11796g. B. M. R.

Category: USSR / Physical Chemistry.   B-8
          Thermodynamics. Thermochemistry. Equilibrium. Physico-
          chemical analysis. Phase transitions.

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29930

Author : Shchukarev S. A., Morozova M. P., Kan Kho-Yn, Kokosh G. V.
Inst   : not given
Title   : Strongtium-Bismuth System

Orig Pub: Zh. obshch. khimii, 1956, 26, No 6, 1525-1531

Abstract: By methods of physico-chemical analysis a study has been made of
          the Sr - Bi system. On the basis of thermal analysis data and distri-
          bution of averaged gram-atomic volumes, it was ascertained that there
          exist the congruent fusible compounds $SrBi_3$, Sr_3Bi_x and Sr_3Bi and the
          incongruent fusible SrBi. Results of microscopic investigation con-
          firm the type of the diagram of state derived by means of the first
          two methods. From values of thermal effect of interaction of SrBi,
          Sr_3Bi_x and Sr_3Bi with dilute HCl (for description of the calorimetric
          procedure see RZhKhim, 1955, 34012) a determination was made of enthalpy

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Card   : 1/2

Category: USSR / Physical Chemistry.
Thermodynamics. Thermochemistry. Equilibrium. Physico-
chemical analysis. Phase transitions.   B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29930

of their formation, $\triangle$ H, which was found to be, respectively, of
-43.0 $\div$ 2.7; -126.8 $\div$ 2.6 and -74.8 $\pm$ 1.2 kcal/g-formula. A compari-
son is presented of the $\triangle$ H values of some binary compounds of ele-
ments of principal subgroup of group V of the periodic system with
alkaline-earth metals.

Card   : 2/2   -46-

USSR/Thermodynamics. Thermochemistry. Equilibria. Physico-Chemical   B-8
          Analysis. Phase Transitions

Abs Jour : Ref Zhur - Khimiya, No 8, 1957, 26101

Author   : S.A. Shchukarev, I.V. Vasil'kova, B.N. Sharupin
Title   : To the Study of Molybdenum Halide. I. Evaporation and Dis-
           sociation Pressure of Molybdenum Pentachloride.

Orig Pub : Zh. obshch. khimii, 1956, 26, No 8, 2093-2097

Abstract : The pressure of the saturated vapor and of dissociation of
           $MoCl_5$ (I) was determined by the flow method in a flow of N_2
           and in the range from 70 to 160°. The following was found
           from the obtained data: $\log p\, I = 10.623 - 3991/T$; $\Delta H^0 =$
           18.3 kcal per mol, $\Delta S^0 = 35.6$ entr. units, $\Delta F^0 = 7.7$ kcal
           per mol. The same for the reaction $2MoCl_5$ (solid) $= 2MoCl_4$
           (solid) $+ Cl_2$ were: $\log k_p = 14.143 - 5412/T$ $\Delta H^0 = 24.5$
           kcal per mol, $\Delta S^0 = 49.2$ entr. units, $\Delta F^0 = 9.9$ kcal per
           mol; and for the reaction $2\,MoCl_5$ (gas) $= 2MoCl_4$ (solid) $+$
           Cl_2: $\log K_p = -6.753 + 2448/T$; $\Delta H^0 = -12.3$ kcal per mol;
           $\Delta S^0 = 50.2$ entr. units; $\Delta F^0 = 2.6$ kcal per mol. The
           heat of formation of I ΔH^0 (form.) $= -78.5$ kcal per mol.

Card   : 1/1

SHCHUKAREV, S, A,

Application of the mass spectrometric method to the study of the evaporation of slightly volatile substances. I. S. A. Shchukarev and G. A. Semenov (A. A. Zhdanov State Univ., Leningrad). *Zhur. Neorg. Khim.* 2, 1217-20(1957).—A variation of the Langmuir method (*C.A.* 8, 870) was used to measure the vapor pressure of BaO, the mass spectrometer being used to measure the intensity of the mol. current. An ionic source was designed with an independent evaporator and ionizer. The effectiveness of ionizing BaO from a W surface at 1660° was detd. to be 5.4 ± 0.3%. The heat of sublimation for BaO measured at 900-1200° was 89 kcal./mole, and the temp. relation of the vapor pressure for the temp. range 900-1200° can be expressed by the equation log $P = -(19,400/T) + 8.89$.   J. R. L.

Shchukarev, S.A.

Oxychloride of trivalent uranium. S. A. Shchukarev and A. I. Efimov. Zhur. Neorg. Khim. 2, 2304-6(1957).—A new compd., uranium oxymonochloride, was described, thus making up a total of five known oxychlorides: UOCl, UO_2Cl_2, $UOCl_2$, $UOCl_3$, and $UOCl_3$. Dark red transparent crystals of UOCl were formed in small amts. during the distn. of UCl_4 contaminated with UO_2 at 1000° under $10^{-4} - 10^{-5}$ mm. pressure. UOCl is insol. and stable in water, BtOH, Me_2CO, and CCl_4. It decompd. at room temp. in dilute H_2SO_4 or HCl with evolution of H. The crystals of UOCl belong to the tetragonal system having the lattice consts. $a = 4.00$ and $c = 6.85$ A.   A. P. Kotlobay—

79-2-1/58

AUTHORS: Shchukarev, S. A.; Morozova, M. P.; Kan Kho Yn.

TITLE: The Enthalpy of Formation of Strontium Phosphide (Ental'piya obrazovaniya fosfida strontsiya)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 2, pp. 289-290 (U.S.S.R.)

ABSTRACT: Strontium phosphide (Sr_3P_2) was obtained during the reaction of phosphorus with metallic strontium. Both these substances were taken in a ratio corresponding to the chemical formula. Heating of the element up to $400 - 450°$ resulted in the absorption of the entire phosphorus by the strontium. The strontium phosphide obtained in such a way was in the form of a fine crystalline dark-grayish powder, unusually sensitive to atmospheric humidity. The enthalpy of the formation of strontium phosphide was established at -235.4, 233.8, -237.3, -237.5, -235.4, i. e., an average of -235.9 ± 2 kcal/g. These enthalpy magnitudes were established on the basis of enthalpy values observed during the reaction of Sr_3P_2 with diluted hydrochloric acid.

Card 1/2   There is one reference, which is Slavic.

79-2-2/58

AUTHORS: Shchukarev, S. A.; Morozova, M. P.; Kan Kho Yn.; Sharov, V. T.

TITLE: The Enthalpy of Formation of Lithium and Barium Bismuthides
              (Ental'piya obrazovaniya vismutidov litiya i bariya)

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 2, pp. 290-293 (U.S.S.R.)

ABSTRACT: Lithium bismuthide (Li_3Bi) was prepared by melting the components,
              taken in a stoichiometric ratio, in a hermetically sealed steel
              crucible at a temperature of 1200°. The compound obtained in such
              a manner was a coarse-crystalline dark-greenish substance. The
              enthalpy value for this compound was fixed at -39.5 ± 0.5 kcal/g.

              The barium bismuthide (Ba_3Bi_2) was prepared by melting the bismuth
              with the barium, obtained by the high vacuum aluminothermy method,
              in a steel crucible at a temperature of 1100°. The enthalpy of

Card 1/2

The Enthalpy of Formation of Lithium and Barium Bismuthides 79-2-2/58

formation of this latter compound was fixed at - 128.1 $\pm$ 1.8 kcal/g.
The bismuthides of both metals appear to be quite typical intermetallic
compounds and the change in the heat of formation, resulting in the
displacement of magnesium by barium, is subject to entirely different
laws. The enthalpy values established were found to be different from
the values established by Kubaschewski and Villa (6).

2 tables, 1 graph. There are 11 references, of which 7 are Slavic.

ASSOCIATION: The Leningrad State University

PRESENTED BY:

SUBMITTED: March 24, 1956

AVAILABLE: Library of Congress

Card 2/2

USSR/Physical Chemistry - Thermodynamics, Thermochemistry,   B-8
          Equilibria, Physical-Chemical Analysis, Phase Transitions.

Abs Jour   : Ref Zhur - Khimiya, No 1, 1958, 352

          character of the chemical bond in compounds were investiga-
          ted. In the opinion of the authors, the rule of the ther-
          mochemical logarithmic curve (Kapustinskiy A.F., Dokl. AN
          SSSR, 1951, 80, 755) is incopatible with the existence of
          the secondary periodicity.

Card 2/2

Shchukarev, S. A.

/Thermodynamic characteristics of the formation of halide complexes of cadmium in aqueous solutions. S. A. Shchukarev, L. S. Lilich, and V. A. Latysheva. Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanova No. 211, Ser. Khim. Nauk No. 15, 17–25(1957).—The dependence of the variations of the oxidation-reduction potential of the system $Cd(Hg)/Cd^{++}$ on the concn. of Cl^-, Br^-, and I^- at 25, 35, and 45° is given. The values of $\Delta F°$, ΔH, ΔS, and standard molar entropy at 25° and ionic strength $\mu = 4.5$ are the following: (species, $\Delta F°$ cal./g. ion, ΔH cal./g. ion, ΔS cal./g. ion degree, $S°$ cal./g. ion degree, resp.). $CdCl^+$, -1800, 0, 6.1, 4.8; $CdCl_2$, -1230, -300, 3.1, 20.9; $CdCl_3$, 120, 2600, 9.2, 43.3; $CdCl_4^{--}$, 620, 2900, 7.7, 64.2; $CdBr^+$, -2300, 2300, 15.4, 20.2; $CdBr_3$, -1000, -4300, -11.1, 27.1; $CdBr_2$, -1100, 2000, 10.4, 58.0; $CdBr_4$, -700, 2600, 11.1, 88.3; CdI^+, -2700, —, —, 21.5; CdI_3, -1100, —, —, 50.7; CdI_3, -3000, —, —, 86.8; and CdI_4^{--}, -2000, —, —, 120.0. The stability consts. are also detd.   A. Libackyl

SOV/54-58-3-12/19

AUTHORS: Shchukarev, S. A., Lilich, L. S., Timofeyev, V. I.

TITLE: The Entropy of the **solution** of Some Salts (Entropiya rastvoreniya nekotorykh soley)

ABSTRACT: The method chosen in the present paper has already been applied in the case of the mixture of two liquids (Refs 4-6). The new feature is its application to the   solution of a solid in a liquid solvent. The authors expressed the thermodynamical functions as   solution functions (n) and not as functions of the molar fraction. This made possible a better approximation to the ideal state in aqueous salt solutions. The   solution entropy was computed for a number of salts (mainly for the halogens of the elements of the I. and II. group of the periodic system) and for a certain range of concentrations. The computed data are given in figures 1 and 2 and in tables 1 and 2. The absolute entropies of some solutions were computed as well (Table 3). From the curves conclusions concerning the thermodynamics of the

Card 1/2

The Entropy of the **Solution** of Some Salts   SOV/54-58-3-12/19

solution and to a certain degree also of the solution
itself can be deduced. According to the relative position
of the three basic thermodynamical functions at least 3
cases are strikingly evident: a) ΔZ and ΔH are in the exo-
thermic and ΔS in the endothermic range; b) ΔZ is in the
exothermic, ΔH and ΔS are in the endothermic range;
c) ΔZ, ΔS, and ΔH are all exothermic. It turned out
that in some cases the enthalpy - the interaction between
the solvent and the substance to be dissolved - plays a
considerable role. In other cases the increase in entropy
of the solvent and of the dissolved substance during their
interaction is decisive. Finally cases exist in which both
factors act in one and the same direction. The suggested
computation method classifies the solutions according to
Mendeleyev's conceptions concerning solutions as belonging
into one line with common chemical compounds. There are 7
figures, 2 tables, and 7 references, 4 of which are Soviet.

SUBMITTED: January 9, 1958

Card 2/2

SOV/54-58-3-18/19

AUTHORS: Shchukarev, S. A.,   Lilich, L. S.,   Timofeyev, V. I.

TITLE: Modification of the Isobaric Potential During the Solution of Some Halides in Water (Izmeneniye izobarnogo potentsiala pri rastvorenii nekotorykh galogenidov v vode)

ABSTRACT: In the present paper the authors computed the change of the isobaric Gibbs potential ΔZ of a number of substances when they are mixed with water. The computed quantities are of practical importance as they characterize the real and practically important formation processes of solutions and their components. In the computation of the change of ΔZ the equation $\Delta Z = \Delta \mu_1 + n \Delta \mu_2$ was used as starting point.

$\Delta \mu_1$ denotes the change of the chemical potential of the dissolved substance at the transition from the pure salt or the saturated solution to the solution of the respective concentration; n denotes the number of moles of the solvent per 1 mol of the dissolved substance; $\Delta \mu_2$ denotes the change

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SOV/54-58-3-18/19

Modification of the Isobaric Potential During the **Solution** of Some
Halides in Water

of the chemical potential of the solvent during the transi-
tion from the pure solvent to the solution in question. The
change of ΔZ (at $T = 25^{\circ}$) during the formation of some
salt solutions (halides of the elements of the I. and II.
group of the periodic system) in the initial state - salt
plus water - was computed.(Tables 1, 2). The integral quan-
tities determined are represented as **solution** functions
of the solutions n . A contrast between the functions
$\Delta Z = f(n)$ permits to draw conclusions on their resemblance
in form and the difference in their relative position. The
latter depends on the chemical individuality of the inter-
acting systems. Some advantages of the employed reading
scale as compared to the usual scale for electrolytic solu-
tions are shown. There are 2 figures, 1 table, and 12 ref-
erences, 7 of which are Soviet.

SUBMITTED: January 9, 1958

Card 2/2

AUTHORS: Shchukarev, S.A., Oranskaya, M.A., $SOV/ 78-3-7-2/44$
             Tolmacheva, T.A., Vanicheva, L.L.

TITLE: The Thermal Dissociation of Gold Bromide (Termicheskaya
             dissotsiatsiya bromidov zolota)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 7, pp. 1478-1482
             (USSR)

ABSTRACT: In the course of the present work the dissociation of $AuBr_3$ in
             the temperature interval 350-450°K was investigated according to
             two static methods: with the isoteniscope and with the isoten-
             iscope with glass membranes. Gold bromide is produced by the
             action of bromine upon pulverized gold. In connection with this
             dissociation it was found that disintegration develops with the
             forming of AuBr and the oxidation of monobromide. For the dis-
             sociation of $AuBr_3$ it holds that: $\lg P_{Br_2} = 8.99 - \dfrac{4052}{T}$ (360-450°K)

             and for the dissociation of AuBr it holds that:

             $\lg P_{Br_2} = 7.39 - \dfrac{3532}{T}$ (360-450°K). On the strength of the results

Card 1/2   obtained the enthalpy and enthropy of the formation of AuBr and

The Thermal Dissociation of Gold Bromide $SOV/78-3-7-2/44$

$AuBr_3$ were calculated for the interval of 350-450°K. The temperature dependence of the energy liberated during the formation of gold halides is given. Radiograms of gold, AuBr and $AuBr_3$ were taken. During the dissociation of gold monobromide the lines of gold and not disintegrated $AuBr_3$ were detected in the samples. It was confirmed by Debyegrams that AuBr is dissociated at low temperatures. It was shown that at temperatures below 325°K AuBr is disproportionated to $AuBr_3$ and Au, and that at room temperatures it exists only in a metastable state. There are 2 figures, 5 tables, and 10 references, 4 of which are Soviet.

SUBMITTED: June 1, 1957

1. Gold bromide--Decomposition   2. Gold bromide--_ _ _ _ _ _ _ factors
3. Gold bromide--Preparation   4. Radiography--Appl_ _ _ _ _ _

Card 2/2

AUTHORS: Shchukarev, S.A., Yakimov, M.A., Mishin, V.Ya. SOV/78-3-7-34/44

TITLE: Investigation of the Solubility in the System $CsNO_3$-HNO_3-H_2O
            at 25° (Issledovaniye rastvorimosti v sisteme $CsNO_3$-HNO_3-H_2O
            pri 25°)

ABSTRACT: Investigations of the solubility of cesium in a nitric acid
            solution by means of radiometric methods were carried out by the
            application of radioactive cesium Cs^{134}.
            Determination of solubility was carried out at $25 \pm 0.05°$ C in
            the course of 3.5-4 hours.
            In a concentrated nitric acid solution (d_4^{15} - 1.43-1.50) the
            acid salt crystallizes with a composition of $CsNO_3 \cdot HNO_3$.
            The stability of this acid salt is between 0° and 50° C. With an
            increase of temperature the quantity of this salt decreases.
            From a 96% nitric acid solution the compound $CsNO_3 \cdot 2HNO_3$ is
            formed at low temperatures. There are 2 figures, 3 tables and
Card 1/2   7 references, 2 of which are Soviet.

Investigation of the Solubility in the System
$CsNO_3-HNO_3-H_2O$ at $25°$

SOV/ 78-3-7-34/44

SUBMITTED: June 8, 1957

1. Cesium--Solubility   2. Nitric acid--Solvent action   3. Cesium
compounds--Analysis   4. Cesium isotopes(Radioactive)--Applications

Card 2/2

AUTHORS: Shchukarev, S. A., Kolbin, N. I.,   SOV/78-5-8-1/48
             Ryabov, A. A.

TITLE: On the Dissociation- and Sublimation Tension of
             Ruthenium-(III)-Chlorine (Ob uprugosti dissotsiatsii i
             sublimatsii trikhlorida ruteniya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, Nr 8,
             pp. 1721-1726 (USSR)

ABSTRACT: $RuCl_3$ is produced by chlorination of finely powdered metallic
             ruthenium with chlorine. For the determination of the dis-
             sociation- and sublimation tension of $RuCl_3$, three methods have
             been used.
             1) Static method with buffer - concentrated sulfuric acid.
             2) Method of the quartz membrane.
             3) Dynamically with nitrogen as carrier gas.
             The dissociation tension of solid ruthenium-(III)-chloride at
             temperatures of 773-1053°K was calculated. From these data
             the variation of the thermodynamic functions with the dis-
             sociation of ruthenium-(III)-chloride was found:
             $\Delta H_{298} = 49 \pm 2$ kcal, $\Delta F_{298} = 35 \pm 2$ kcal, $\Delta S_{298} = 47 \pm 2$ e.u.

Card 1/2

On the Dissociation- and Sublimation Tension   SOV/78-3-6-
of Rhenium-(III)-Chloride

The sublimation of $RuCl_2$ was determined at $850-1100°K$. On the strength of these results the thermodynamic characteristic values of the sublimation process of $RuCl_3$ for the temperature $975°K$ were calculated. $\Delta H = 46$ kcal, $\Delta S = 41$ e.u. There are 3 figures, 5 tables, and 8 references, 4 of which are Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet, Kafedra obshchey
                 i neorganicheskoy khimii (State University of Leningrad,
                 Chair of General and Inorganic Chemistry)

SUBMITTED   July 8, 1957

Card 2/2

AUTHORS: Shchukarev, S. A., Novikov, G. I., Suvorov, A. V., Bayev, A. K.

TITLE: Optical and Tensiometric Investigation of the Chlorides of
                Hexavalent Tungsten (Opticheskoye i tenzimetricheskoye
                issledovaniye khloroproizvodnykh shestivalentnogo vol'frama)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12,
                pp 2630-2641 (USSR)

ABSTRACT: Several equilibria pertaining to the chlorine derivatives of
                hexavalent tungsten in the series WO_3-WO_2Cl_2-$WOCl_4$-WCl_6 were
                investigated. Optical and tensiometric methods were used in
                determining the products of the thermal decomposition. The
                starting materials were produced by chlorinating WO_3 with CCl_4.
                At 310-330°C WO_2Cl_2 is obtained in ratio to the WO_3 and CCl_4
                of 1:2. WCl_6 is produced at 290-300° and 80-100 atmospheres.
                The purity of the starting product was found to be satisfactory.
                The absorption spectra of the WCl_6 and $WOCl_4$ were measured

Card 1/3   over the interval 4000-8000 Å. The optical density of the vapor
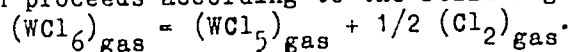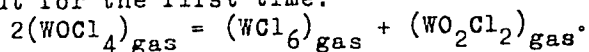
SOV/78-3-12-7/36

Optical and Tensiometric Investigation of the Chlorides of Hexavalent Tungsten

phase from the decomposition of the WCl_6 was measured. The decomposition proceeds according to the following equation:
$$(WCl_6)_{gas} = (WCl_5)_{gas} + 1/2 (Cl_2)_{gas}.$$
The absorption coefficient x_{WCl_6} was determined for the saturated vapor, and the average value was found to be 0.46 ± 0.05. From the tensiometric data the melting and boiling temperatures of the β-form of WCl_6 could be calculated. Using the optical and tensiometric methods the thermodynamic investigation of the following disproportionation process was carried out for the first time:
$$2(WOCl_4)_{gas} = (WCl_6)_{gas} + (WO_2Cl_2)_{gas}.$$
From the optical and tensiometric data for the saturated vapors and using the linear relationship $\lg P = f(1/T)$ and $\lg D = f(1/T)$ it was found that the absorption coefficient $x_{WOCl_4} = 0.028\pm0.3$. The change in the free energy in this reaction is expressed in the following equation: $\Delta F^0_{solid} = 15100$ cal -

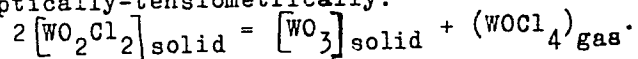Card 2/3   13,4 energy units . . .T. The following disproportionation

Optical and Tensiometric Investigation of the Chlorides of Hexavalent Tungsten

process of WO_2Cl_2 was investigated thermodynamically and con-
firmed optically-tensiometrically:

$$2\left[WO_2Cl_2\right]_{solid} = \left[WO_3\right]_{solid} + \left(WOCl_4\right)_{gas}.$$

The change in free energy in the process is expressed in the
following equation: $\Delta F^{o}_{solid} = 29100 \text{ cal} - 42.9 \text{ cal/degree(en.ed.)}$
.T. The results show that the optical and tensiometric methods
can be applied successfully to the determination of the partial
composition of complicated gas systems. There are 11 figures,
8 tables, and 15 references, 6 of which are Soviet.

SUBMITTED: September 5, 1957

Card 3/3

SOV/78-3-12-8/36

AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Novikov, G. I.
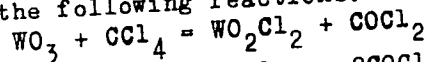
TITLE: III. The Determination of the Heat of Formation of Chlorine Derivatives of Hexavalent Tungsten (III. Opredeleniye teplot obrazovaniya khlorproizvodnykh shestivalentnogo vol'frama)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12, pp 2642-2646 (USSR)

ABSTRACT: The heat of solution of $WOCl_4$, WO_2Cl_2, and WCl_6 in 12% NaOH and at 25°C was determined. The production of the initial materials was carried out by chlorinating WO_3 with CCl_4 according to the following reactions:

$$WO_3 + CCl_4 = WO_2Cl_2 + COCl_2$$
$$WO_3 + 2CCl_4 = WOCl_4 + 2COCl_2$$
$$WO_3 + 3CCl_4 = WCl_6 + 3COCl_2$$
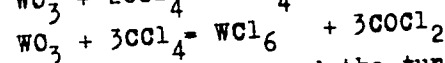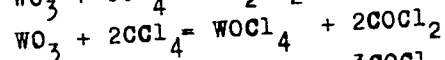
In all the compounds investigated the tungsten is hexavalent. The oxychlorides $WOCl_4$ and WO_2Cl_2 dissolve more quickly than WCl_6 in the 12% NaOH solution. The following values were found

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SOV/78-3-12-8/36

III. The Determination of the Heat of Formation of Chlorine Derivatives of Hexavalent Tungsten

for the respective heats of formation of WCl_6, $WOCl_4$, and WO_2Cl_2: -163.1, - 177.5 and -199 kcal/mole. The heats of formation of the chlorides and oxides of the elements of the fifth group in the periodic system were compared and for chromium, molybdenum, tungsten, and uranium almost equal values were found for the $\Delta H_{formation}$ for MeO_2Cl_2 and corresponding oxides MeO_3. There are 1 figure, 4 tables, and 12 references, 6 of which are Soviet.

SUBMITTED: August 5, 1957

Card 2/2

SOV/78-3-12-9/36

AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Martynova, N. S.,
            Mal'tsev, Yu. G.

TITLE: Concerning the Heat of Formation of Uranyl Chloride and Mono-
            Oxyuranyl Trichloride (O teplote obrazovaniya uranilkhlorida i
            monooksitrikhlorida urana)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12,
            pp 2647-2650 (USSR)

ABSTRACT: The heat of   solution of UCl_4, UO_2Cl_2, and $UOCl_3$ in a 0.5%
            $FeCl_3$ and 2% HCl solution was determined. The synthesis of the
            starting materials is described. The results for the heats of
            dissolution are given in table 2:
            ΔH for $FeCl_3$ in 2% HCl = -30.75 ± 0.27 kcal/mole
            ΔH for UO_2Cl_2 in 0.5% $FeCl_3$ in 2% HCl = -25.44 ± 0.07 kcal/mole
            ΔH for UCl_4 in 0.5% $FeCl_3$ in 2% HCl = -45.50 ± 0.10 kcal/mole
            ΔH for $UOCl_3$ in 0.5% $FeCl_3$ in 2% HCl = -28.55 ± 0.13 kcal/mole.

Card 1/2   The standard heat of formation for UO_2Cl_2 and $UOCl_3$ was

SOV/78-3-12-9/36

Concerning the Heat of Formation of Uranyl Chloride and Mono-Oxyuranyl Tri-chloride

calculated: $\Delta H_{formation} UO_2Cl_2$ = -301.9 kcal/mole and

$\Delta H_{formation} UOCl_3$ = -283.4 kcal/mole.

There are 2 tables and 9 references, 4 of which are Soviet.

SUBMITTED: September 5, 1957

Card 2/2

SOV/78-3-12-10/36

AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Drozdova, V. M.

TITLE: The Heat of Formation of Uranyl Bromide and Mono-Oxy Uranyl Tribromide (Teplota obrazovaniya uranilbromida i monooksitribromida urana)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12, pp 2651-2653 (USSR)

ABSTRACT: The heat of   solution was determined for UO_2Br_2 and $UOBr_3$ in a 0.5% $FeCl_3$ and 2% HCl solution. The synthesis of the UO_2Br_2 and $UOBr_3$ is described. The UO_2Br_2 was produced by the oxidation of UBr_4 in an oxygen stream at 160-165°, and the $UOBr_3$ was produced by reacting water-free uranium trioxide with CBr_4. The heat of formation for UO_2Br_2 and $UOBr_3$ is determined by taking the difference between the heats of dissolution of the compounds under investigation. At 25° the heat of formation of uranyl bromide $\Delta H = -31.23 \pm 0.20$ kcal/mole, of $UOBr_3$ $\Delta H = -45.42 \pm 0.21$ kcal/mole. For the heat of formation at 298°K
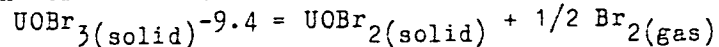
Card 1/2

SOV/78-3-12-10/36

The Heat of Formation of Uranyl Bromide and Mono-Oxy Uranyl Tribromide

for mono-oxy uranyl tribromide ΔH was found to be -233.8 kcal/mole and for $UO3r_2$ ΔH was found to be 254.2 kcal/mole.

From the heats of formation so obtained for $UOBr_3$ and $UOBr_2$ the ΔH for the dissociation reaction

$$UOBr_{3(solid)}{}^{-9.4} = UOBr_{2(solid)} + 1/2\ Br_{2(gas)}$$

was calculated.

There are 1 table and 8 references, 3 of which are Soviet.

SUBMITTED: September 5, 1957

Card 2/2

SHCHUKAREV, S.A.; LILICH, L.S.; TIMOFEYEV, V.I.

Entropy of a solution of various salts [with summary in English].
Vest. LGU 13 no.16:105-111 '58.   (MIRA 11:11)
(Solution (Chemistry))   (Entropy)

SHCHUKAREV, S.A.; LILICH, L.S.; TIMOFEYEV, V.I.

Changes in the isobaric potential during the dissolving of some
halides in water [with summary in English]. Vest. LGU 13 no.16:
149-155 '58.   (MIRA 11:11)
        (Halides)   (Solution (Chemistry))

AUTHOR: Shchukarev, S. A.   79-28-3-52/61

TITLE: On the Number of Stable Oxides Formed by the Metals of the
            Great Periods of the Periodic System(O chisle ustoychivykh
            okislov, obrazuyemykh metallami bol'shikh periodov sistemy)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 3, pp. 795-811
            (USSR)

ABSTRACT: This work is a continuation of the work published by the
            author in 1945 (reference 1). The thermodynamic field of exi-
            stence of any one   oxidation stage has characteristic
            features which are dependent most exactly on the interactions
            between the members of the whole pleiad of binary compounds
            formed of two simple bodies. In considering the pleiad of
            gaseous oxides it can be seen that the great energies of the
            atomization of the simple bodies decrease in width the dia-
            pason of the resistivity in the oxide pleiad of the given
            element. A certain part is played by the principle of the
            even and odd number of molecules as well as by the polymeri-
            zation of the compounds when single oxidation stages are
Card 1/3   dropped. It is shown that a great part of the oxides of all

On the Number of Stable Oxides Formed by the Metals of the Great   79-28-3-52/61
Periods of the Periodic System

metals of the even series of the great periods within the
system can be modified in gaseous state and that they disso-
ciate. The known rule by Beyl on the displacement of the
high oxidation stages of the upper pleiad boundary, i.e. ab-
ove the binding of the highest d-metal oxides in the motion
from above to below in the vertical series of the system is
explained by the concept   of the energy amplification of
the condensation of the highest oxides as well as that of the
attenuation of the endo-effect of the gradual saturation of
the atoms of the metal with oxygen. The author points out to
new rule for the jump to the higher stages of oxidation of
the lower limit of resistance in the pleiad in the series
motion within the system from above to below, which is ex-
plained by the metal atomization. With an oxide of highest
condensation energy (e.g. OsO_2) there is shown a tendency
towards the precipitation of the neighbouring higher or low-
er oxide from the pleiad thanks to the formation of the dis-
proportion_alities of the phenomena. The mentioned rules can
be used not only with oxides but also with compounds of
other classes as well as with bodies in solution. There are

Card 2/3   8 figures, 9 tables, and 7 references, 4 of which are Soviet.

On the Number of Stable Oxides Formed by the Metals of the   79-28-3-52/61
Great Periods of the Periodic System

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad
                State University)

SUBMITTED: March 11, 1957

Card 3/3

AUTHOR: Shchukarev, S. A.

79-28-4-1/60

TITLE: On the Basic and Acid Anhydrides of the Metals of the
               Great Periods of Systems (Ob osnovnykh i kislotnykh
               okislakh metallov bol'shikh periodov sistemy)

PERIODICAL: Zhurnal Obshchey Khimii, 1958 Vol. 28, Nr 4.
               pp. 845 859 (USSR)

ABSTRACT: Energetic characteristics are not complete and the
               situations b in the transitions from the compounds with
               an ion binding to materials with a covalent binding as
               well as the reciprocal reactions of the oxides with water
               play an important rôle in the problem of basicity and
               acidity of the oxides. However, thermodynamical interac=
               tions, already because of the great number of experimental
               quantity values, may play an important part. As a concrete
               example the author has investigated the behaviour of va=
               nadium which, as is known produces V_2O_5, VF_5, VBr_3 and
               VJ_2 in the highest oxidation phases.

Card 1/4   1) The thesis on the exceeding of the formation enthalpy

On the Basic and Acid Anhydrides of the Metals   79-28-4-1/60
of the Great Periods of Systems

of chloride of the corresponding metal over the formation
enthalpy of the oxide (of the same oxidation stage) may
serve for the characteristics of the basic oxide. When
the formation enthalpy of the oxide considerably exceeds
the formation enthalpy of the corresponding chloride the
oxide tends to hydrolysis and can be characterized as
a chloride. In the case of near values of the formation
enthalpies of chloride and oxide the latter will be am=
photeric. 2) A metal which is able to form a series of
oxidation phases has the following curves representing
the dependence of $\Delta H_{stand.}$ (standardized energy of for=
mation) on the oxidation stages: the chloride curve is
lower than the curve of the basic oxides in the lower
oxidation phases. later on, after the intersection of
the curves (in the amphoteric oxide) the chloride curve
is above the oxide curve (in the higher oxidation phases).
This rule can be used for the evaluation of the formation
enthalpies of little known oxides and chlorides. 3) If
the curves of the formation enthalpies (computation per
1 gram atom of the oxidizable element) of the highest
oxides and chlorides of the elements which are in the same
Card 2/4   order of the system are plotted intersections of the cur=

On the Basic and Acid Anhydrides of the Metals   79-28-4-1/60
of the Great Periods of Systems

ves can be observed. The oxides TiO_2, V_2O_5, CrO_3, Mn_2O_7
prove to be acid due to these intersections; therefore,
acidity of Mn_2O_7 is in connection with the fact that Mn
can form an oxide of a high - seventh - oxidation stage.
4) The explanation of the just demonstrated reciprocal
situation of the curves does not only depend on the energies
of the interatomic bindings but: a) on the endo effect of
the ion formation $O^=$ which reduces the formation enthalpy
of the basic (lowest) oxides; b) on the endo effect of the
coordination of the chlorine atoms near the central atom,
which reduces the formation enthalpy of the high chlorides;
c) on the fact that with increasing number of oxidation
phases the exoeffect of condensation energy of the gaseous
compounds decreases much more rapidly with chlorides than
with oxides. 5) Neutralization of the basic oxides with
acid anhydrides (CO_2, N_2O_5) depends on the trend of the

Card 3/4   electrons toward dissipation, i. e. not toward accumulation

On the Basic and Acid Anhydrides of the Metals
of the Great Periods of Systems   79-28-4-1/60

to one and the same atom ($O^=$, $N^=$ etc.) but to distribution
to various atoms of a polyatomic anion. This is energeti=
cally favorable. The same reason - the disadvantage of accu=
mulation of negative charges in one and the same atom-leads
to a decrease of the formation enthalpies from chlorides to
oxides, nitrides and carbides 6) An explanation of the
trends of the element form especially stable compounds on the
formation of materials with the formula AB, which was already
mentioned by D. I. Mendeleyev, is given. 7) It is said that
the endo effect of coordination increases: a) from fluori=
des to iodides; b) from the elements of the VIth period to
the elements of the IVth period; c) from Ca to Ni, from Sr
to Pd and from Ba to Pt. 8) The endo effect of the coordi=
nation of hydrogen atoms is much smaller than that of fluorine
atoms.

There are 8 figures, 5 tables and 4 references, 3 of which
are Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State
University)

SUBMITTED: March 12, 1957

Card 4/4

SOV/79-28-7-63/64

AUTHORS: Shchukarev, S. A., Novikov, G. I., Andreyeva, N. V.

TITLE: Letter to the Editor (Pis'mo v redaktsiyu). On the Problem Concerning the Thermodynamic Investigation of the Lowest Tungsten Chlorides (K voprosu o termodinamicheskom issledovanii nizshikh khloridov vol'frama)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 7, pp. 1998 - 1999 (USSR)

ABSTRACT: The authors determined by means of the membrane zero reading manometer produced of quartz the pressures of the saturated and unsaturated vapor of tungsten pentachloride according to the static method. They found according to the optical tensometric method that the gaseous tungsten pentachloride disproportionates under the formation of tungsten tetra- and tungsten hexachloride. By the direct determination of the molecular weight of the vapor of tungsten pentachloride they found 10% W_2Cl_{10}.

According to the same method with the quartz membrane they determined the disproportioning pressures of WCl_2 and WCl_4.

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SOV/79-28-7-63/64

Letter to the Editor. On the Problem Concerning the
Thermodynamic Investigation of the Lowest Tungsten Chlorides

1. Tungsten chlorides--Thermodynamic properties   2. Tungsten chlorides--Vapor pressure
3. Vapor pressure--Determination

Card 3/3

SOV/79-28-12-29/41

AUTHORS: Shchukarev, S. A., Morozova, M. P., Borzakova, M. M.

TITLE: Formation Enthalpy of Cadmium Compounds With Phosphorus, Arsenic and Antimony (Ental'piya obrazovaniya soyedineniy kadmiya s fosforom, mysh'yakom i sur'moy)

ABSTRACT: Earlier the authors (Ref 1) showed that the process of heat formation of the compounds of nitrogen, phosphorus, arsenic, antimony and bismuth with zinc, contrary to that of the compounds of these elements with magnesium or strontium, takes place according to the rule of secondary periodicity (Ref 1). The authors were interested in finding the magnitudes of the heat of formation of cadmium compounds with the elements of the main subgroup of group (V). With nitrogen cadmium forms the extremely unstable compound CdN_2 (Ref 2), with phosphorus Cd_3P_2, and apparently the unstable phosphide which probably possesses the formula CdP_2 (Ref 3). In the system cadmium-arsenic the compound Cd_3As_2 (Refs 3-5), and in the system cadmium-antimony the compounds $CdSb$ and Cd_3Sb_2 were found. Compounds of

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SOV/79-28-12-29/41

Formation Enthalpy of Cadmium Compounds With Phosphorus, Arsenic and Antimony

cadmium with bismuth are not present, at least in the thermo-dynamical sense of the word. The elements that had been chemically purified and investigated by spectrum analysis were used for the syntheses of the preparations. The formation enthalpy constants of Cd_3P_2, Cd_3As_2, and Cd_3Sb_2 were determined. It turned out that in spite of the heats of formation of the similar zinc and cadmium compounds, which are very close to each other, there exists a marked difference between the various formation heat constants of their compounds with the elements of the main subgroup of group (V). The substitution of cadmium for zinc in these compounds is accompanied by an abrupt decrease of the formation heats. The process of heat formation of the compounds of cadmium with the elements of the main subgroup of group (V) is obeying the rule of the secondary periodicity. There are 1 figure, 2 tables, and 14 references, 5 of which are Soviet.

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SOV/79-28-12-29/41

Formation Enthalpy of Cadmium Compounds With Phosphorus, Arsenic and Antimony

ASSOCIATION: Leningradskiy gosudarstvennyy universitet
(Leningrad State University)

SUBMITTED: November 16, 1957

Card 3/3

SOV/20-120-5-36/67

AUTHORS: Shchukarev, S. A., Semenov, G. A.

TITLE: Mass-Spectrometer Investigation of Germanium Dioxide Sublimation
             (Mass-spektrometricheskoye izucheniye sublimatsii dvuokisi
             germaniya)

PERIODICAL: Doklady Akademii nauk SSSR, Vol. 120, Nr 5, 1955,
             pp. 1059 - 1061 (USSR)

ABSTRACT: The semiconductor properties of germanium are highly dependent
             upon its surface state as a surface film is formed by its
             compounds. They arouse a growing interest. The vapor tension
             of germanium and its sublimation heat have hitherto not been
             measured at all. From the point of view mentioned at the
             beginning the knowledge of the thermodynamical characteristics
             of germanium dioxide is very essential. Davydov (Ref 1) ascribed
             an abrupt change of the sublimation temperature between
             886 - 980° and 1025 - 1078° to a phase transition at 1000°. In
             previous experiments the amount of the sublimation heat of
             silver was determined. In the mass spectrum of the silver vapors
             only Ag^+-ions were found. Table 1 shows data on the mass spectrum
             of the vapor above GeO_2. The intensities which correspond to

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Mass-Spectrometer Investigation of Germanium Dioxide   S07/2o-12o-5-36/67
Sublimation

the individual germanium isotopes were added and referred to
the stream of ions of $Ge_3O_3^+$ the intensity of which was set
equal to unity. $Ge_3O_2^+$- and GeO_2^+ -ions were observed as well the
ion current of which amounted to approximately 0,5% of the
amount of the current of $Ge_3O_3^+$. Figure 1 shows a part of the
mass spectrum which corresponds to the ion groups $Ge_2O_2^+$ and
$Ge_3O_3^+$. For several groups of the spectrum the enthalpies in
kcal/mol were determined and calculated according to the slope
of the straight line
$lg(I^+T) = f(\frac{1}{T})$. Within the limits of experimental error the
authors did not notice breaks in the straight line. The
magnitude of the vapor tension may be evaluated from the com-
parison of the ion currents of $Ge_3O_3^+$ and Ag^+. The ratio of the
effective cross-sections of the ionization for the Ge_3O_3-molecule
and the Ag-atom approaches the value of 4:1 (Ref 6). In this
case the following assumption

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Mass-Spectrometer Investigation of Germanium Dioxide   SOV/20-120-5-36/67
Sublimation

$$I_1^+T_1 = \frac{I_2^+T_2}{4} = kP$$ is justified. $I_1^+T_1$ and $I_2^+T_2$ are in a corresponding ratio to the ion currents of Ag^+ and $Ge_3O_3^+$. The equation of this type applies to the ion source used here (which did not differ on principle from that of Aldrich, Ref 2), e.g. in the case of

$T_1 = 1073^o$ and $T_2 = 1338^o$. With silver a vapor of $6 \cdot 10^{-5}$ torr, (Refs 4,5) corresponds to a temperature of 800°. As a consequence it will be of an order of $2 \cdot 10^{-2}$ torr for Ge_3O_3 at 1065°. Thus the composition of the gaseous phase in the evaporation of germanium dioxide proves to be analogous to that found in the evaporation of SiO_2 (Refs 7,8). There are 1 figure, 1 table, and 9 references, 3 of which are Soviet.

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Mass-Spectrometer Investigation of Germanium Dioxide   SOV/2o-12o-5-36/67
Sublimation

ASSOCIATION: Leningradskiy gosudarstvennyy universitet im.A. A.Zhdanova
               (Leningrad State University imeni A.A.Zhdanov)

PRESENTED: February 5, 1958, by A.N.Terenin, Member, Academy of Sciences,
               USSR

SUBMITTED: January 24, 1958

               1. Germanium oxides--Sublimation   2. Germanium vapors--Mass spectrum
               3. Ionic current--Measurement   4. Semiconductors--Properties

Card 4/4

PHASE I BOOK PUBLICATION

24(8)

Akademiya nauk SSSR. Otdeleniye khimicheskikh nauk

Termodinamika i stroyeniye rastvorov; trudy soveshchaniya... (Thermodynamics and Structure of Solutions; Transactions of the Conference held January 27-30, 1958) Moscow, Izd-vo AN SSSR, 1959. 295 p. 3,000 copies printed.

Ed.: M. I. Shakhparonov, Doctor of Chemical Sciences; Ed. of Publishing House: M. G. Yegorov; Tech. Ed.: T. V. Polyakova.

PURPOSE: This book is intended for physicists, chemists, and chemical engineers.

COVERAGE: This collection of papers was originally presented at the Conference on Thermodynamics and Structure of Solutions sponsored by the Section of Chemical Sciences of the Academy of Sciences, USSR, and the Chemistry Department of Moscow State University, and held in Moscow on January 27-30, 1958. Officers of the conference are listed in the Foreword. A list of other reports also read at the conference, but not included in this book, are given. Among the problems treated in this work are: electrolytic solutions, ultrasonic measurements, spectro-scopic analysis, etc. References accompany individual articles. and thermodynamic properties of various mixtures, dielectric

5(2), 5(3)

AUTHORS: Shchukarev S. A. Vasil'kova I. V., Sharupin, B. N.

TITLE: II. On the Investigation of Molybdenum Haloids. Determination of the Formation Enthalpy of Some Chlorine Derivatives of Penta-valent and Hexavalent Molybdenum (II. K issledovaniyu galidov molibdena. Opredeleniye ental'pii obrazovaniya nekotorykh proizvodnykh pyati- i shestivalentnogo molibdena)

ABSTRACT: In this paper the authors determined the formation enthalpy of $MoCl_5$, MoO_2Cl_2 and $MoOCl_4$ according to the difference in enthalpy of the reactions of these compounds and MoO_3 with 0.7-8 n NaOH. The reaction enthalpy of the following four reactions was determined by means of a calorimeter with an isothermal shell:

$$MoO_3 + 2NaOH - 18.60 \text{ kcal} = Na_2MoO_4 + H_2O \qquad (1)$$

$$MoCl_5 + 1/2H_2O_2 + 7NaOH - 179.01 \text{ kcal} = Na_2MoO_4 + 5NaCl + 4H_2O \qquad (2)$$

$$MoO_2Cl_2 + 4NaOH - 62.64 \text{ kcal} = Na_2MoO_4 + 2NaCl + 2H_2O \qquad (3)$$
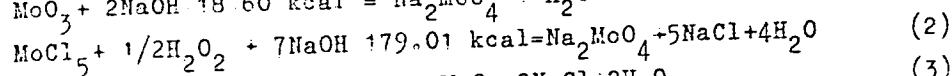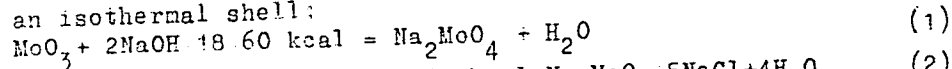
Card 1/3

SOV/54-59-1-9/25

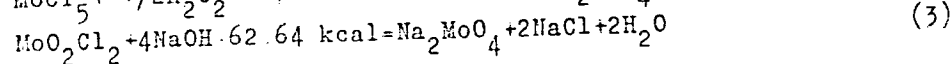II On the Investigation of Molybdenum Haloids. Determination of the Formation Enthalpy of Some Chlorine Derivatives of Pentavalent and Hexavalent Molybdenum

in 1931. The value of ΔH_{MoO_3} which was found in this paper and forms the basis of the respective calculations, amounts to 3.60 kcal/moles. There are 2 figures, 3 tables, and 11 references, 3 of which are Soviet.

SUBMITTED: March 24, 1958

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SOV/54-59-1-7/25

5(3)
AUTHORS: Shchukarev, S. A., Novikov, G. I., Andreyeva, N. V.

TITLE: Thermodynamic Investigation of Lower Tungsten Chlorides
              (Termodinamicheskoye issledovaniye nizshikh khloridov vol'frama)

PERIODICAL: Vestnik Leningradskogo universiteta. Seriya fiziki i khimii,
              1959, Nr 1, pp 120-131 (USSR)

ABSTRACT: For these investigations compounds WCl_5 and WCl_4 were used,
              which were obtained from WCl_6 by reduction with hydrogen WCl_2
              was obtained from the decomposition of WCl_4 in vacuum at $450°$
              (Refs 1,4) The three tungsten chlorides were analyzed by vapor
              hydrolysis, a method that had been worked out by the authors in
              their work as per reference 9 The vapor pressure of WCl_5 was
              determined in the temperature range of $150-800°$ The values for
              the saturated and unsaturated vapor pressures are given in
              table From the latter the molecular weight of WCl_5 in the
              vapor phase was determined by the aid of the Mendeleyev-
              Klapeyron equation In this connection the presence of dimers

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SOV/54-59-1-17/25

Thermodynamic Investigation of Lower Tungsten Chlorides

was detected in the vapor and the thermodynamic characteristics of dipolymerization, proceeding according to the scheme $(W_2Cl_{10})_{vapor} = 2(WCl_5)_{vapor}$, were calculated. The total pressure and the optical density of WCl_5 in the temperature range of $150-500°$ were measured (measuring results in table 3). These measurements led to the assumption that tungsten pentachloride is disproportionated according to the scheme $2(WCl_5)_{vapor} = (WCl_4)_{vapor} + (WCl_6)_{vapor}$. For this process the thermodynamic characteristics were determined by approximation. From the pressure of the saturated vapor of WCl_5 also the thermodynamic characteristics of sublimation and of evaporation were determined together with the melting and boiling point temperatures. It was further found that WCl_4 is likewise disproportionated, the disproportionation pressure having been measured in the temperature range of from 300 to $600°$. Disproportionation is according to the scheme $3 WCl_4 \, solid = WCl_2 \, solid + 2(WCl_5)_{vapor}$, WCl_4

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SOV/54-59-1-17/25

Thermodynamic Investigation of Lower Tungsten Chlorides

evaporating simultaneously. From the data obtained from the pressure measurements the thermodynamic characteristics were determined for this disproportionation process as well. The disproportionation pressure for the solid WCl_2 was measured in the temperature range of from 490 to 580^0 (Table 14). There are 15 tables and 15 references, 6 of which are Soviet.

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SOV/54-59-2-9/24

5(2,4)
AUTHORS: Shchukarev, S. A., Lilich, L. S., Latysheva, V. A.,
             Chuburkova, I. I.

TITLE: On the Heats of Reaction of CdO and $Cd(OH)_2$ With Hydrogen
             Halides and Perchloric Acids (O teplotakh vzaimodeystviya CdO
             i $Cd(OH)_2$ s galogenovodorodnymi i khlornoy kislotami)

ABSTRACT: From the measurements of the heats of reaction of metal oxides
             and their hydrates, information is obtained on the state of the
             ions in solutions. The method of this investigation consists in
             determining the heat effects of individual processes in the re-
             action of metal hydroxides and oxides with the acids. (Destruc-
             tion of the oxide lattice, dissociation of the acid, formation
             of H_2O molecules from the H^+ and OH^- ions, and formation of
             complexes between the ions of the metal, of the water and the
             anions of the acids.) As in the investigations of the present
             paper only one metal was used, the difference in the heat ef-
             fects lies only in the complex formation and is dependent on

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On the Heats of Reaction of CdO and Cd(OH)$_2$ With Hydrogen Halides and Per-
chloric Acids

SOV/54-59-2-9/24

the various acids used. The perchloric acid which shows no
tendency to form a complex was assumed as a zero solvent. The
Cd-hydroxides and oxides were synthesized in a crystalline
form, and checked for purity by means of X-rays and chemically.
The measurements of the heats of reaction of the mentioned
crystals with the solvents HCl, HBr, HJ, and HClO$_4$ were carried
out at 25° with various concentrations of the latter. The
results are compiled in a table and represented in a figure.
The values of J. Thomsen (Ref 5) are also indicated for com-
parison. The table and the figure show that at low concentra-
tions of HCl and HBr the reaction proceeds endothermically,
at an increase in concentration, however, it becomes exo-
thermal. The minimum shifts from HCl to HBr to lower concentra-
tions. In case of HJ, there is nearly no minimum at all. The
HClO$_4$ solution produces a straight line which becomes ther-
mically more and more negative with an increase in concentra-
tion. There is a good agreement of the values obtained for the
two former solutions with the values of Thomsen, but a

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On the Heats of Reaction of CdO and Cd(OH)$_2$ With Hydrogen Halides and Perchloric Acids

noticeable deviation in case of HJ. Thomsen used solutions in the stoichiometric ratio G$^-$: Cd^{++}, whereas in this paper this ratio was varied between 20 and 400 with an excess in G$^-$ (G$^-$ = halogen ion). The values obtained were also compared with values of other authors who determined the formation heats by other methods (Refs 9-15). As in previous papers (Ref 2), the hydration heat of Cd^{++} was computed by the formula: h$_{Cd}$$^{++}$ = -ΔH+U$_o$-2h$_{OH}$$^-$ + 2H. In this formula, ΔH = heat effect of the reaction: Cd(OH)$_2$ + HClO$_4$, U$_o$ = lattice energy of the hydroxide, h$_{OH}$$^-$ = hydration heats of the OH$^-$-ions, H = heat effect of the formation of H$_2$O from the hydrated ions. The value 437.5 kcal/g-ion is obtained. This value is in good agreement with the values known from publications. Yatsimirskiy (Ref 18): h$_{Cd}$$^{++}$ = 436 kcal/mol, and Mishchenko and Podgornaya (Ref 20): 445 kcal/mol. There are 1 figure, 1 table, and 20 references, 8 of which are Soviet.

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On the Heats of Reaction of CdO and Cd(OH)$_2$ With Hydrogen Halides and Per-
chloric Acids

SUBMITTED: January 18, 1958

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SOV/54-59-2-10/24

5(4)
AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Sharupin, B. N.

TITLE: On the Investigation of Molybdenum Halides. Synthesis and Determination of Formation Enthalpy of Molybdenum Tetrachloride (K issledovaniyu galidov molibdena. Sintez i opredeleniye ental'pii obrazovaniya tetrakhlorida molibdena)

PERIODICAL: Vestnik Leningradskogo universiteta. Seriya fiziki i khimii, 1959, Nr 2, pp 72-77 (USSR)

ABSTRACT: In this paper, which represents part of the dissertation by B. N. Sharupin, a checking of the value of the formation enthalpy of the molybdenum tetrachloride was carried out. In a previous paper (Ref 4), the dissociation enthalpy of the $MoCl_5$ had been computed by use of tensimetrical data from the reaction: $[MoCl_5] + 12.2$ kcal $= [MoCl_4] + 1/2\ Cl_2$ (1). The formation enthalpy ΔH of the $MoCl_5$ was assumed with -90.8 kcal/mol according to references 5,1,2. The value obtained for ΔH of the $MoCl_4$ agreed with the corresponding values of the mentioned papers. A new measurement by the authors (Ref 6), how-

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On the Investigation of Molybdenum Halides. Synthesis and Determination of
Formation Enthalpy of Molybdenum Tetrachloride

ever, yielded the value: -126 kcal/mol for the ΔH_{form} of the
$MoCl_5$. In order to discover the causes of this discrepancy,
the formation enthalpy was computed from the data of a method
principally different from reference 6, and checked in this
way. ΔH was determined by the difference of the reaction
enthalpies of $MoCl_5$ and $MoCl_4$ with solutions containing
0.5% $FeCl_3$ and 2% HCl. The investigations were carried out at
25°C. To investigate a possible disproportionation of $MoCl_4$ in
the presence of trivalent iron in $MoCl_3$ and $MoCl_5$, and a fur-
ther oxidation of the ion Mo^{3+} to Mo^{5+}, the optic density of
the solution obtained in the calorimeter was determined
(Fig 1). This showed that in this solution only the pentavalent
molybdenion was present. (For the synthesis of $MoCl_5$, see ref-
erence 4.) The synthesis of $MoCl_4$ was carried out on the plant
represented in figure 2. The best conditions for the synthesis

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On the Investigation of Molybdenum Halides. Synthesis and Determination of
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proceeding according to the reaction: $Mo+O_2+2CCl_4=MoCl_4+2COCl_2$
are: temperature of furnace 300°, temperature of the saturator
25°, and velocity of nitrogen 5-6 l/hour. 5-6 g $MoCl_4$ were ob-
tained in this way in 8 hours. The determination of the
enthalpy is described in the papers (Refs 6,12). The values of
the reaction enthalpies of $MoCl_4$ and $MoCl_5$ with the mentioned
solution are compiled in tables 1,2. The computation of the
formation enthalpy of $MoCl_4$ was carried out on the basis of the
following reactions: $MoCl_5+H_2O(0.5\%\ FeCl_3,\ 2\%\ HCl)=MoOCl_3+2HCl$;
$MoCl_4+FeCl_3+H_2O=MoOCl_3+HCl+FeCl_2$. The formation enthalpy of the
components of this reaction is indicated in table 3, taken from
the papers (Refs 6,12,2). The formation enthalpy for $MoCl_4$ was
determined at $-(114\pm3)$ kcal/mol. This value coincides with the
value obtained in the paper (Ref 6) from tensimetric data for
the dissociation reaction of $MoCl_5$ and its formation enthalpy.

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On the Investigation of Molybdenum Halides. Synthesis and Determination of Formation Enthalpy of Molybdenum Tetrachloride

There are 2 figures, 3 tables, and 12 references, 5 of which are Soviet.

SUBMITTED: April 5, 1958

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SOV/54-59-2-11/24

5 (4)
AUTHORS: Shchukarev, S. A., Novikov, G. I.,
Andreyeva, N. V.

TITLE: Dependence of the Disproportionation Pressure of Low Tungsten
Chlorides on the Composition of the Solid Phase
(Zavisimost'uprugosti disproportsionirovaniya nizshikh
khloridov vol'frama ot sostava tverdoy fazy)

PERIODICAL: Vestnik Leningradskogo universiteta. Seriya fiziki i khimii,
1959, Nr 2, pp 78-82 (USSR)

ABSTRACT: The thermodynamic characteristic of the disproportionation of
WCl_4 and WCl_2 to the final products WCl_2, and metallic W
respectively, is only possible if in the existing solid phase
no interaction of these substances occurs. In this connection,
investigations of the dependence mentioned in the title were
carried out here. WCl_6 was used as initial product for the
preparation of the low tungsten chlorides. WCl_4 was obtained
by repeated reduction (Refs 3-5) in the dry hydrogen current,
and WCl_2 by disproportionation of the latter. The initial

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Dependence of the Disproportionation Pressure of
Low Tungsten Chlorides on the Composition of the Solid Phase

mixture used for the investigation, which contained WCl_5, WCl_4
and WCl_2 and also metallic W, was analyzed by pyrolysis
(Ref 6). The results are indicated in table 1. The steam
pressure over the mixture was statically determined by a
quartz-diaphragm zero manometer (see Refs 7, 8). The total
pressure of the steam over a WCl_5 + WCl_4 mixture with
different ratios Cl:W at different temperatures (Table 2)
shows that the isothermal line of the steam pressure at the
interval 4.6-4.0 Cl:W assumes the values of the isothermal
line of the disproportionation pressure of the pure WCl_4.
This statement shows that there is a certain limited solubility
between WCl_5 and WCl_4. The insolubility of the mentioned
substances in one another is determined by the pressure of the
disproportionated steam over the WCl_4 + WCl_2 mixture at
various ratios Cl:W (Table 3) which shows perfectly horizontal
isothermal lines. Table 4 shows the disproportionation

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Dependence of the Disproportionation Pressure of   SOV/54-59-2-11/24
Low Tungsten Chlorides on the Composition of the Solid Phase

pressures of the steam over a mixture of WCl_2 + metallic W.

It shows that there is a certain interaction between the
mentioned substances. A comparative X-ray investigation
showed that WCl_2 exists in the range 2.0-1.7, and some
unknown lines can be observed beside the lines of the latter;
in the range 1-0, there are only the lines of pure metallic
tungsten beside some unknown lines. Therefore, the deter-
mination of the disproportionation scheme of the mixture
WCl_2 is rendered very difficult by the existence of a
solubility of WCl_2 and W in one another. There are 4 tables
and 8 references, 3 of which are Soviet.

SUBMITTED: June 4, 1958

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SOV/30-59-3-59/61

5(0)
AUTHORS: Shchukarev, S. A., Doctor of Chemical Sciences, Makarenya, A. A.
             - (Abstracters)

TITLE: New Edition of the Works by D. I. Mendeleyev on the Periodic System
             (Novoye izdaniye rabot D. I. Mendeleyeva po periodicheskomu zakonu)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, Nr 3, pp 141-143 (USSR)

ABSTRACT: This is a review of the reference work by D. I. Mendeleyev
             mentioned in the title.- There is 1 Soviet reference.

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SOV/78-4-1-7/48

5(2), 21(1)
AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Drozdova, V. M., Martynova, N. S.

TITLE: III. The Energetics of Solid Uranium Oxyhalides in the Light of the Substitution Principle (III. Energetika tverdykh oksigalidov urana v svete printsipa zameshcheniya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 1, pp 33-38 (USSR)

ABSTRACT: The ΔH value for the formation of UBr_4 was determined and it was found that this value is -214.9 kcal/g-atom in contrast to the value -211.3 kcal suggested by D. Kats and Ye. Rabinovich (Ref 6). This value was found by determining the solution heat of UBr_4 and UCl_4 in hydrochloric acid solutions of iron chloride. The value ΔH for the formation of UBr_4 was determined according to the reaction $U_{solid} + 2Br_{2gas} = UBr_{4solid}°$ Figure 1 shows the formation enthalpies of the chlorides, bromides, oxides, oxychlorides, and oxybromides of uranium. The figure shows that the curves of the solid oxides are lower than

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III. The Energetics of Solid Uranium Oxyhalides in the Light of the Substitution Principle

those of the solid chlorides and especially of the bromides (with the exception of UCl_2). With regard to energetics and the exchange principle the situation of the oxychlorides has to be regarded as intermediary between halides and oxides. The comparative proximity of the curves of the chlorides and oxides as compared to the curves of the bromides and oxides can be explained by the fact that oxygen and chlorine have about the same oxidation properties. The formation enthalpies of solid oxyhalides are higher than those of the solid oxides and therefore the oxyhalides have more energy. The exchange energetics are determined by simple regularities with regard to the theory of chemical compounds. The greater condensation energy of oxychlorides shows that these compounds are more stable than oxides and that they show less dismutation trend. There are 2 figures, 1 table, and 8 references, 5 of which are Soviet.

SUBMITTED: August 6, 1957

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SOV/78-4-1-8/48

5(4), 21(1)
AUTHORS: Shchukarev, S. A., Vasil'kova, I. V., Drozdova, T. M.,
                Frantseva, K. Ye.

TITLE: The Determination of the Formation Heat of UO_2Cl_{2aqu}, UO_2Br_{2aqu},
                $UO_2Cl_2 \cdot H_2O$, $UO_2Cl_2 \cdot 3H_2O$, $UO_2Br_2 \cdot H_2O$ and $UO_2Br_2 \cdot 3H_2O$
                (Opredeleniye teplot obrazovaniya UO_2Cl_{2aq}, UO_2Br_{2aq},
                $UO_2Cl_2 \cdot H_2O$, $UO_2Cl_2 \cdot 3H_2O$, $UO_2Br_2 \cdot H_2O$ i $UO_2Br_2 \cdot 3H_2O$)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 1, pp 39-41
                (USSR)

ABSTRACT: The crystal hydrates of uranyl chloride and uranyl bromide
                were produced from anhydrous UO_2Cl_2 and UO_2Br_2 by treatment
                with inert gas containing steam at room temperature. The
                synthesized compounds were analyzed by the determination of
                uranium according to th Vanadate method. The chlorine and
                bromine content was determined. The determination of the
                solution heat of anhydrous uranyl chloride and uranyl bromide
                and their monohydrates and trihydrates in water at infinite
                dilution was carried out at 25°. The results are shown in

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The Determination of the Formation Heat of UO_2Cl_{2aqu}, UO_2Br_{2aqu}, $UO_2Cl_2 \cdot H_2O$, $UO_2Cl_2 \cdot 3H_2O$, $UO_2Br_2 \cdot H_2O$ and $UO_2Br_2 \cdot 3H_2O$

table 2. The following values were given:

$\Delta H\ UO_2Cl_2 = -23.86 \pm 0.13$ kcal/mol

$\Delta H\ UO_2Cl_2 \cdot H_2O = -13.32 \pm 0.23$ kcal/mol

$\Delta H\ UO_2Cl_2 \cdot 3H_2O = -10.00 \pm 0.11$ kcal/mol

$\Delta H\ UO_2Br_2 = -33.28 \pm 0.32$ kcal/mol

$\Delta H\ UO_2Br_2 \cdot H_2O = -24.42 \pm 0.08$ kcal/mol

$\Delta H\ UO_2Br_2 \cdot 3H_2O = -21.51 \pm 0.12$ kcal/mol

On account of the values of the solution heat the formation heat of UO_2Cl_{2aqu}, UO_2Br_{2aqu}, $UO_2Cl_2 \cdot H_2O$, $UO_2Cl_2 \cdot 3H_2O$, $UO_2Br_2 \cdot H_2O$, and $UO_2Br_2 \cdot 3H_2O$ was calculated and summed up in table 3. The values of the formation heat of UO_2Cl_{2solid} and UO_2Br_{2solid} are as follows:

$\Delta H_{formation(298^\circ K)} UO_2Cl_{2solid} = -301.9$ kcal/mol

$\Delta H_{formation(298^\circ K)} UO_2Br_{2solid} = -281.6$ kcal/mol.

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The Determination of the Formation Heat of UO_2Cl_{2aqu}, UO_2Br_{2aqu}, $UO_2Cl_2 \cdot H_2O$, $UO_2Cl_2 \cdot 3H_2O$, $UO_2Br_2 \cdot H_2O$ and $UO_2Br_2 \cdot 3H_2O$

The dehydration heat of $UO_2Cl_2 \cdot 3H_2O$ was calculated according to the following equation: $UO_2Cl_2 \cdot 3H_2O = UO_2Cl_2 \cdot H_2O + 2H_2O_{gas}$. This value is in accordance with the value obtained by the tensimetric method (Ref 4). There are 3 tables and 6 references, 4 of which are Soviet.

SUBMITTED: September 5, 1958

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SOV/78-4-7-41/44

5(2)
AUTHORS: Shchukarev, S. A., Kolbin, N. I., Ryabov, A. N.

TITLE: On a Volatile Higher Chloride of Ruthenium (O letuchem vysshem khloride ruteniya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 7, pp 1692-1693 (USSR)

ABSTRACT: The authors found in the course of the chlorination of metallic ruthenium by means of chlorine gas that amorphous $RuCl_3$ is deposited at the cold places of the apparatus. As the vapor pressure of $RuCl_3$ is negligibly low at the temperature of $400°$ used, this cannot concern the evaporation of $RuCl_3$. The formation of $RuCl_4$ is assumed and its vapor pressure is calculated from the difference between the $RuCl_3$ carried away in the nitrogen- and in the chlorine current. The investigation is being continued. There are 1 figure and 2 references, 1 of which is Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet im. Zhdanova, Kafedra neorganicheskoy khimii (Leningrad State University imeni
Card 1/2

On a Volatile Higher Chloride of Ruthenium   SOV/78-4-7-41/44

            Zhdanov, Chair for Inorganic Chemistry)

SUBMITTED: February 23, 1959

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5(2)

SOV/78-4-9-22/44

AUTHORS: Shchukarev, S. A., Novikov, G. I., Suvorov, A. V., Maksimov, V. K.

TITLE: The Thermographical Investigation of the Systems WCl_6 - WO_3, WCl_6 - WO_2, WCl_6 - $MoCl_5$

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 9, pp 2062-2066 (USSR)

ABSTRACT: Tungsten oxychlorides are only occasionally described in publications. However, as tungsten forms a considerable number of oxides and chlorides, a corresponding number of oxychlorides may be expected. The equipment used in the investigation is schematically drawn in figure 1. One of the thermograms drawn by means of two M-21 reflecting galvanometers is given in figure 2 as an example. A scheme of the electric furnace is shown in figure 3. Figure 4 represents the melting-point diagram of the system WCl_6 - WO_3. From this it is evident that two oxychlorides are formed in the system $WOCl_4$ and WO_2Cl_2. From the melting-point diagram of the system WCl_6 - WO_2 (Fig 5) three hitherto unknown oxychlorides were deduced:

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The Thermographical Investigation of the Systems   SOV/78-4-9-22/44
$WCl_6 - WO_3$, $WCl_6 - WO_2$, $WCl_6 - MoCl_5$

$3WCl_6 \cdot WO_2$, $WCl_6 \cdot WO_2$ (or $WOCl_3$), and $WCl_6 \cdot 3WO_2$. A simple eutectic
and regions of partial solubility in the solid phase were
ascertained in the melting-point diagram of the system
$WCl_6 - MoCl_5$ (Fig 6). There are 6 figures and 5 references,
1 of which is Soviet.

SUBMITTED: June 16, 1958

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SOV/78-4-10-1/40

5(2)
AUTHORS: Shchukarev, S. A., Novikov, G. I., Kokovin, G. A.

TITLE: Determination of Saturation Vapor Pressure and Molecular
              Weight of Tungsten Pentabromide

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 10,
              pp 2185-2188 (USSR)

ABSTRACT:
There are only a few data available in publications on the
bromine compounds of tungsten presently known (WBr_6, WBr_5,
WBr_2, $WOBr_4$, WO_2Br_2). For this reason the authors report on
tensimetric and thermographic determinations carried out on
WBr_5. $W(CO)_6$ and Br_2 were used as initial products, which re-
act under formation of hexabromide which was decomposed in
vacuo at 250° to give WBr_5 and Br_2. The tensimetric determi-
nation was carried out by means of a diaphragm-zero-manometer
made of heat-resistant glass of the P-15 type. The temperature
was measured by means of the PPTV-1 potentiometer. Table 1
gives the values obtained for the vapor pressure of WBr_5 between
170.4 and 384.4°C and 1 - 655 torr. In figure 1 the curve

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Determination of Saturation Vapor Pressure and Molecular Weight of Tungsten Pentabromide

$\log P_{saturated} = f(\frac{1000}{T^{\circ}K})$ is shown. Between 230° and the melting point 295°C the values are below the calculated curve owing to impurities. The computed values for the vaporization and sublimation enthalpy and -entropy are in good agreement with the values obtained by L. Brewer (Ref 1), whereas the resultant melting- and boiling points deviate from the data available in publications. According to table 3 the analysis of WBr_5 gives a bromine content somewhat higher than that corresponding with the formula which is due to bromine adsorption. The values computed at $678.2^{\circ}K$ and $742.2^{\circ}K$ for the molecular weight of WBr_5 are likewise above the theoretical value. The presence of polymerized molecules is assumed. The solidification temperature obtained by tensimetry deviates a little from the value determined thermometrically (Table 5). There are 1 figure, 5 tables, and 6 references, 2 of which are Soviet.

SUBMITTED: June 1, 1957

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SOV/78-4-10-5/40

5(2).
AUTHORS: Shchukarev, S. A., Lilich, L. S., Latysheva, V. A.,
                Andreyeva, D. K.

TITLE: On the Heats of Interaction of HgO With Aqueous Solutions of
                HCl, HBr, HJ, and HClO$_4$

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 10,
                pp 2198-2203 (USSR)

ABSTRACT: This paper is a continuation of the papers of references 1-3
                on the heats of interaction of oxides and hydroxides of the
                metals of the 2nd group of the periodic system with halogen
                hydracids and chloric acid. The authors try to evaluate the
                total variation (ΔH) of enthalpy on formation of halogen com-
                plexes by comparison of the heat of interaction of the metal
                oxide with complex-forming acids (HCl, HBr, HJ) and with HClO$_4$
                which is not complex-forming. So far Ba, Cu^{II}, Zn and Cd have
                been investigated. The investigation of the interaction of HgO
                now presented permits a comprehensive survey regarding the
                behavior of the zinc-subgroub. The dependence of ΔH_{298} on the

Card 1/3   acid concentration (1-4 mole/l) is presented in table 1 and

On the Heats of Interaction of HgO With Aqueous Solutions of HCl, HBr, HJ,
and HClO$_4$

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figure 1. The dependence on kind and concentration of the anions is determined by complex formation. The formation of mercury-halogen complexes is exothermic in the concentration range investigated. The heat of hydration of the Hg^{2+}-ion calculated to be 441 kcal/mole is in good agreement with the data in publications (Table 2). With increasing atomic number of the cation of the zinc-subgroup and of the anion of the chlorine-subgroup the endothermic nature of the complex formation decreases and the exothermic nature increases (Table 3). With increasing atomic number of the cation also the difference between the formation enthalpies of the Cl-, Br-, and J-complexes increases (Fig 2). A secondary periodic dependence between the atomic numbers of the metal and the influence of the acidity upon the enthalpy of the interaction between the oxides (hydroxides) of Zn, Cd, Hg and chloric acid was found to exist (Fig 3). This dependence is explained by a different weakening of the interaction of the cations with the water, similar to that observed by O. Ya. Samoylov (Ref 16) in the system alkaline earth chloride - hydrochloric acid. The concentration of the hydracids affects the nature of the dependence of the enthalpy of the complex compounds on the atomic number of the

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On the Heats of Interaction of HgO With Aqueous Solutions of HCl, HBr, HJ, and $HClO_4$

cation. There are 3 figures, 3 tables, and 18 references, 12 of which are Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet im. A. A. Zhdanova Kafedra neorganicheskoy khimii (Leningrad State University imeni A. A. Zhdanov, Chair of Inorganic Chemistry)

SUBMITTED: July 20, 1958

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SOV/78-4-11-43/50

5(2)
AUTHORS: Shchukarev, S. A., Semenov, G. A., Frantseva, K. Ye.

TITLE: The Mass Spectrometric Investigation of the Sublimation of Some Oxides of Vanadium and Niobium

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 11, p 2638 (USSR)

ABSTRACT: The composition of the vapor over VO_2, V_2O_3 and NbO_2 was investigated in the evaporation of the oxides on a platinum film in an ion source as described in reference 1 at an ionization voltage of 50 v. In the evaporation of VO_2 and NbO_2, the ions VO_2^+ and NbO_2^+ predominate, the ions VO^+ in the case of V_2O_3. A table gives the intensities of the ionization currents at 1500 - 1800°K as well as the sublimation energies. The deviation of the sublimation energy found for V_2O_3 with 111±2 kcal/mol from the data by J. Berkovitz, W. A. Chupka and M. G. Inghram (Ref 2) for the process $[VO] \longrightarrow (VO)$

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The Mass Spectrometric Investigation of the
Sublimation of Some Oxides of Vanadium and Niobium

is assumed to be due to the circumstance that no VO develops in the solid phase of V_2O_3, and the value found is influenced by secondary processes. The dissociation energy of VO_2 was found to be in good agreement with reference 2 and amounting to 12.7 ev. The dissociation energy of NbO_2 was equal to 14.8 ± 0.5 ev. There are 1 table and 2 references, 1 of which is Soviet.

SUBMITTED: May 11, 1959

Card 2/2

SHCHUKAREV, S.A.; NOVIKOV, G.I.; ANDREYEVA, N.V.

Thermodynamic investigation of the lower tungsten chlorides.
Vest.LGU 14 no.4:120-131   '59.   (MIRA 12:5)
                    (Tungsten chlorides)

SHCHUKAREV, S.A.; LILICH, L.S.; LATYSHEVA, V.A.; CHUBURKOVA, I.I.

Heat of reaction of CdO and Cd(OH)$_2$ with hydrogen halides and perchloric acid. Vest.LGU 14 no.10:66-71 '59.

(MIRA 12:6)

(Cadmium oxide) (Cadmium hydroxide) (Heat of reaction)

SHCHUKAREV, S.A.; VASIL'KOVA, I.V.; SHARUPIN, B.N.

Investigation of molybdenum halides. Synthesis of molybdenum tri-
chloride and the determination of its heat of formation. Vest.LGU
14 no.10:72-77 '59.   (MIRA 12:6)
                 (Molybdenum chlorides)

SHCHUKAREV, S.A.; NOVIKOV, G.I.; ANDREYEVA, N.V.

Effect of the composition of the solid phase on the disproportiona-
tion pressure of lower tungsten chlorides. Vest.LGU 14 no.10:
78-82 '59.   (MIRA 12:6)
                    (Tungsten chlorides)

24 (7), 5 (4)
AUTHORS: Suvorov, A. V., Shchukarev, S. A.,
             Novikov, G. I.

SOV/48-23-10-30/39

TITLE: On the Possibility of a Molecular Spectral Analysis of Vapors
             Within a Wide Temperature Range

ABSTRACT: For the analysis of gas- and vapor mixtures it is possible to
             use the spectrum of this mixture in the visible-, in the
             ultraviolet-, or in the infrared range; whereas in the ultra-
             violet range the quantum energies are already so high that
             un-called-for photochemical reactions occur, the strong
             influence exercised by temperature in the infrared range is a
             disturbing factor. For the investigation of a complex system
             in equilibrium, a spectroscopic method is, in any case,
             insufficient, because it is necessary, besides the partial
             component pressures, to know also the total pressure in the
             system. For their determination it is possible to employ any
             statistical method, but the membrane method (with zero
             manometer) was found to be especially useful. It was found
             that the amount of absorption is influenced by pressure, and

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On the Possibility of a Molecular Spectral Analysis of   SOV/48-23-10-30/39
Vapors Within a Wide Temperature Range

still more by temperature. The temperature dependence of the amount of absorption has hitherto not been quantitatively investigated. Such an empirical method was the aim to be fulfilled by the authors. An investigation of the temperature-dependent variation of absorption and optical density in iodine vapors resulted in the formula $K_y = x_y T$, where x_y is a quantity which is independent of temperature. For its verification the system $N_2O_4 - NO_2 - NO - O_2$ was investigated in the range 18-480 °C. Figure 3 shows the measured temperature dependence of the pressure p and of the optical density D. The diagram may be divided into 3 ranges: I) 18-100°, equilibrium $N_2O_4 = 2NO_2$, II) 100-200°, pure NO_2, III) 200-480°, equilibrium $2NO_2 = 2NO + O_2$. By using the Lambert-Beer law a formula may be derived for the determination of x_y: $x_y = (D_y/p)(R/d)$.

For a given frequency the following is thus obtained:

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x_{5575} = 0.0194 ± 0.0002. Similar investigations were carried out of a number of gas mixtures: WCl_6 - WCl_5 - Cl_2; $WOCl_4$ - WO_2Cl_2 - WCl_6 - Cl_2 and WO_2Cl_2 - WO_3 - $WOCl_4$ - WCl_6 - Cl_2. For the system $WOCl_4$ - WCl_6 - WO_2Cl_2 the temperature dependence of p and D is also shown by a diagram in figure 4. There are 4 figures and 1 Soviet reference.

ASSOCIATION: Khimicheskiy fakul'tet Leningradskogo gos. universiteta im. A. A. Zhdanova (Chemical Department of Leningrad State University imeni A. A. Zhdanov)

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SHCHUKAREV, S.A., doktor khim. nauk; MAKARENYA, A.A.

New publication of the works of D.I. Mendeleev on the periodic
law ("Periodic law" by D.I. Mendeleev. Reviewed by S.A. Shchukarev
and A.A. Makarenia). Vest. AN SSSR 29 no.3:141-143 Mr '59.
                                              (MIRA 12:4)
            (Mendeleev, Dmitrii Ivanovich, 1834-1907)
                    (Periodic law)

5 (2)
AUTHORS: Shchukarev, S. A., Morozova, M. P.,   SOV/79-29-8-1/81
             Li Miao-hsiu

TITLE: The Formation Enthalpy of Titanium Compounds With the Elements
             of the Main Subgroup of Group V

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2465 - 2467
             (USSR)

ABSTRACT: Among the titanium compounds only titanium nitride is investi-
             gated thermochemically (Ref 1). Metallic, spongy titanium
             (99% Ti), carefully purified red phosphorus, arsenic purified
             by distillation, and metallic antimony and bismuth with slight
             impurities of other elements were used as initial products.
             The preparation and the degree of purification of titanium
             phosphide, -antimonide, and -arsenide are described in detail.
             The X-ray photographs of the substances obtained, with the ex-
             ception of titanium bismuthide, which could not be prepared,
             differed only slightly from those mentioned in publications
             (Table 1). The heats of formation were determined by the dif-
             ference between the heats of combustion of the stoichiometric
             mixtures and of the above compounds under equal conditions.
             The heats of combustion are shown in table 2. The combustion

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The Formation Enthalpy of Titanium Compounds With   SOV/79-29-8-1/81
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products of the compounds and the corresponding mixtures were
identical according to radiographic determination (the in-
complete calorimetric combustion of titanium up to TiO_2 in-
fluenced the final result only slightly) (Figure). It may
easily be seen that the process of heat formations is subject
to the law of secondary periodicity (Refs 8,9). In connection
with the results of previous papers (Ref 9) it was ascertained
that among the compounds of the elements of the main subgroup
of group V with metals, the dependence on the above law holds
also for the heats of formation of the compounds with metals
of side groups (Zn,Cd,Ti). The process of the heats of forma-
tion of the compounds of the elements of the main subgroup of
group V on contact with the active metals of such main groups
as Mg,Ca,Sr,Li is not typical of the secondary periodicity.
There are 1 figure, 2 tables, and 9 references, 5 of which are
Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State
University)
SUBMITTED: July 16, 1958
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5 (2)
AUTHORS: Shchukarev, S. A., Andreyev, S. N.,   SOV/79-29-8-2/81
Borisova, Z. U.

TITLE: On the Enthalpy of Dissolution of the Hexahydrate of Zinc
Perchlorate

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2468 - 2470
(USSR)

ABSTRACT: Exact data on the heat of the solution process of various crys-
tallo-hydrates are material for the elaboration of the thermo-
dynamic theory of the solubility of salts, as well as for the
concept of the chemical nature of the crystal hydrates them-
selves. Nothing has hitherto been published on the heats of
solution of the hexahydrate $Zn(ClO_4)_2 \cdot 6H_2O$, which is therefore
the task of the present paper. Preparation and analysis of the
above hydrate are described in detail. In the dissolution of
this freshly precipitated hydrate, containing a small excess of
mother liquor, comparatively low heats were obtained, as may be
seen from figure 1. As was expected, this excess of mother liq-
uor decreases numerically the endothermic effect of the solu-
tion of the salts, since the dilution of the saturated solution

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On the Enthalpy of Dissolution of the Hexahydrate of   SOV/79-29-8-2/81
Zinc Perchlorate

is an exothermic process. The hydrate desiccated within 24 hours
contained 6 molecules of water and yielded a maximum heat of
solution, its value approaching closely that obtained by the
methods described above. This heat decreases numerically with
further desiccation. The data given show that a minimum of de-
hydration, within the limit of error, leads to a considerable
decrease of the heat of solution. The experimental data lead to
the conclusion that the preparation desiccated within 24 hours
is most useful for the determination of the heat of solution.
The values obtained for this heat at various dilutions are
shown in table 2 and in figure 2 (dilutions 1 : 1000 to 1 : 7).
There are 2 figures, 2 tables, and 4 Soviet references.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State
University)

SUBMITTED: June 10, 1958

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SOV/79-29-9-71/76

5(2)

AUTHORS: Shchukarev, S. A., Morozova, M. P., Li Miao-hsiu

TITLE: Enthalpy of Formation of Calcium Compounds With the Elements
   the Main Subgroup of Group V

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,
             pp 3142 - 3144 (USSR)

ABSTRACT: The preparations Ca_3Sb_2 and Ca_3Bi_2 necessary for the investi-
             gation were produced by synthesizing the components taken in
             stoichiometric ratio. Initial products were metallic calcium,
             antimony, and bismuth distillated in high vacuum which, accord-
             ing to the data of spectrum analysis, contained small impurities
             of other metals. Calcium antimonide was produced in a corundum
             pot which was placed into a hermetically sealed steel cylinder
             at 1300°, and calcium bismutide in a hermetically sealed steel
             pot at 1000°. The free space in the pots was filled up with
             argon. Analysis of the compounds proved that the proportion
             of the components did not change in the synthesis, and that
             there are practically no iron and no other steel components
             present. Calcium phosphide and calcium arsenide were prepared

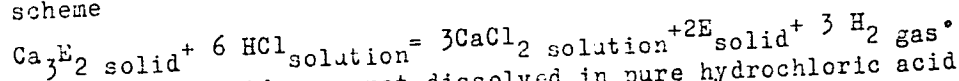Card 1/3   by extended heating of the calcium in phosphorus vapors or,

Enthalpy of Formation of Calcium Compounds with the Ele- SOV/79-29-9-71/76
ments of the Main Subgroup of Group V

accordingly, in arsenic vapors. The excess of nonmetallic
element was separated by heating the preparations in vacuum
(data of analysis). The reaction of calcium phosphide (or
-arsenide) with 1 n. hydrochloric acid was used as calorimetric
reaction (in accordance with the method of reference 1). The
reactions of calcium phosphide and -arsenide proceed quantita-
tively according to the general scheme

$$Ca_3E_2 \text{ solid} + 6HCl \text{ solution} = 3 CaCl_2 \text{ solution} + 2 EH_3 \text{ gas},$$
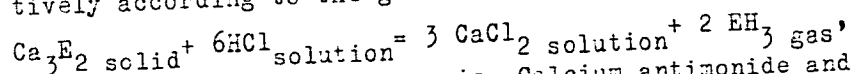
where E = phosphorus or arsenic. Calcium antimonide and calcium
bismutide with hydrochloric acid react according to the general
scheme

$$Ca_3E_2 \text{ solid} + 6 HCl \text{ solution} = 3CaCl_2 \text{ solution} + 2E \text{ solid} + 3 H_2 \text{ gas}.$$

Calcium antimonide was not dissolved in pure hydrochloric acid
solution in the calorimeter, but in a solution in which a certain
amount of calcium antimonide had been solved before. The suspend-
ed and fine-disperse antimony present in such a solution guarant-
ees, as a catalyst in the decomposition of stibine (SbH_3),

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Enthalpy of Formation of Calcium Compounds With the Ele-   SOV/79-29-9-71/76
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practically a complete absence of the latter in the liberated
hydrogen. The values of the heat of solution of the reactions
investigated are listed in the table. On the basis of the known
thermal values of the formation $HCl_{solution}$, $CaCl_{2\ solution}$,
$PH_{3\ gas}$ (Ref 3) and the thermal value of the formation of
arsine recently determined (Ref 4), the above-mentioned values
yield the enthalpies of the formation of calcium compounds with
the elements of the main subgroup of group V which are mentioned on page 3143.
The heats of formation of the calcium compounds in elements
of main group V do not follow the rule of secondary periodicity.
There are 2 figures, 1 table, and 11 references, 9 of which are
Soviet.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State
University)

SUBMITTED: July 16, 1958

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